



## Short communication

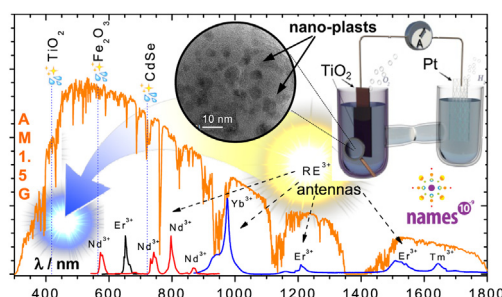
## Rare-earth doped nano-glass-ceramics for extending spectral response of water-splitting semiconductor electrodes by high intense UV-blue up-conversion: Turning the sun into blue

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## HIGHLIGHTS

- High efficient IR to UV-blue up-conversion in rare-earth doped nano-glass-ceramics.
- Long wavelength harvesting of unused portions of solar irradiation.
- Enhanced spectral response of water-splitting semiconductor electrodes of a PEC cell.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The use of hydrogen to feed Fuel Cells emerges as an attractive renewable solution to meet the terawatt carbon-neutral energy demand challenge. Rare-earth doped nano-glass-ceramics, presenting outstanding high intense UV-blue up-conversion processes, appear as an interesting approach to assist long wavelength light harvesting of solar irradiation, extending the photo-catalytic response to the red and near-infrared region to overcome the drawback of large band-gap materials used in the splitting of water into oxygen and hydrogen in a photo-electrochemical cell.

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## 1. Introduction

"Nature! We are surrounded and embraced by her. She is incessantly speaking to us, but betrays not her secret" [1]. In 1912, Giacomo Ciamician stated in his forewarning paper [2], that "human industry will master the photochemical process that hitherto have been the guarded secret of the plants, and this issue should

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not be postponed to distant times, for nature is not in a hurry and mankind is!" Talking about hurry, it should be mentioned that on 8th July 2012, measurements from three satellites from NASA showed that about 40% of the ice sheet had undergone thawing at or near the surface. In just a few days, the melting had dramatically accelerated and an estimated 97% of the ice sheet surface had thawed by July 12th. This unprecedented ice sheet surface melt just proves to us that the Global Warming seems to be real, and large scale of ice melting can occur. And what is more important is that we are in a hurry. On the other hand the increase in the power demand and the likely demise of fossil fuel supplies within the next few decades has led to the development of renewable energy sources and other green technologies. Unfortunately renewable energies use to depend on the variability of source (wind, sun, etc...) and hence, the development of efficient Energy Storage Systems (ESS) is mandatory to provide stable and reliable power. It is estimated that 8% of the world power production should be kept in EES to compensate power peaks and, with the rising introduction of renewable energies this value is expected to increase.

In this context, an attractive solution is the use of the hydrogen, which involves a specific cycle of production, storage and conversion. The energy produced from the sun can be used to split the water and the resulting hydrogen can be stored as compressed gas, liquid hydrogen, or as a metallic hydride, etc. When needed it can provide power through simple combustion or from highly efficient Fuel Cells [3,4]. Fuel Cells appear as reliable systems for power production. They are robust, modular, quiet devices, producing electricity, heat and water as final by-product when hydrogen is used as fuel, contributing to reduce greenhouse gases and pollution. In this way, Daniel G. Nocera [5] demonstrated a very promising step with his artificial photosynthetic leaf [6] to bring cost-effective personalized energy to the non-legacy world. Hence bio-inspiration of photosynthesis leads the way for solar-driven-hydrogen energy renewal source.

In July 1972, Fujishima and Honda demonstrated in their pioneer work in Nature [7] that water could be split into oxygen and hydrogen if the energy of light was used effectively in a photo-electrochemical cell. In particular, UV-blue photons for wavelengths shorter than 415 nm, that is 3.0 eV, which correspond to the band gap of the  $\text{TiO}_2$  electrode, gave rise to the flow of anodic current. Since then, significant efforts have been made during the last 40 years exploring semiconductor engineering, through band gap narrowing by element doping or introduction of defects states, in order to red shift the absorption of semiconductor electrode for matching the maximum of solar spectrum, including the design of complex nanostructures or the  $\text{TiO}_2$  coupling with narrow band gap semiconductors such as CdSe [8]. In that sense, very recent advances achieved in red anatase  $\text{TiO}_2$  microspheres, by means of suitable heteroatoms introduction, for harvesting the full spectrum up to 700 nm exhibiting photo-electrochemical water-splitting under visible light irradiation [9] and in other red metallic oxide photocatalysts [10] ( $\text{Sr}_{1-x}\text{NbO}_3$ ) also extending absorption energy gap to the red.

However, it should be noticed here that up-conversion luminescent materials [11–13], with their ability to transform the unused infrared into available UV light, are very recently becoming a hot focus of investigation to satisfy the genuine requirement of  $\text{TiO}_2$  and other semiconductor electrodes to boost their photo-catalytic action [12,14] in water-splitting as a complementary pure photonic approach to the problem.

It is known that spectral shift of solar irradiation by means of photon up-conversion processes has been already extensively developed, in particular, to increase efficiency in photovoltaic solar cells [15–17]. In that respect, rare-earth (RE) doped nano-glass-ceramics [18,19] appear as one of the most promising candidates

to assist long wavelength light harvesting of solar irradiation, extending the photo-catalytic response of water-splitting semiconductor electrodes to the red and near-infrared region, as green chlorophyll antenna of plants do. These photon-conversion processes appear to be useful to adapt incident solar spectrum into the required blue region, needed for outstanding and best-performing mesoscopic  $\text{TiO}_2$  electrode [20]. Combined with the perfect counterpart, Fuel Cells [3,4], constitute a renewal energy system based on water and sun as overall driving force [21–23]. These processes would help in matching solar spectrum with different semiconductor band gaps used in photo-electrochemical cells and eventually increase the efficiency in solar-driven  $\text{H}_2$  generation. The concept of wavelength shifting through photon-conversion processes has also been used to enhance sunlight harvesting to increase production in agriculture [24], setting the basis for the feasibility of our approach. S. Lian et al. [24] used the luminescent properties of phosphors (in particular alkaline-earth sulphide doped with copper or europium cations) to improve the sunlight conversion efficiency of the photosynthetic process, converting unused portions of sunlight to blue and red light. So water-splitting, as the upfront step of the photosynthesis process, can be also enhanced by shifting solar spectrum in a solely photonic approach to the problem. It was proved that the growth rate of two different crops increased by 23.9 and 21.3%, demonstrating that due to the enhanced sunlight conversion by the phosphors, significant gain in production can be achieved for agricultural plants [24].

Thus, the work presented here explores more suitable candidates towards this goal and makes an additional significant contribution by means of nano-glass-ceramics comprising heavy RE-doped fluoride nanocrystals (i.e.,  $\text{PbF}_2$ ,  $\text{NaYF}_4$ ,  $\text{YF}_3$  and  $\text{KYF}_4$ ) which display high-efficient UV-blue up-conversion emissions, and therefore provide extra photons for absorption by large band gap semiconductors electrodes for water-splitting in a photo-electrochemical cell, i.e., rare-earth nano-plasts antennas for turning the sun into blue.

## 2. Experimental

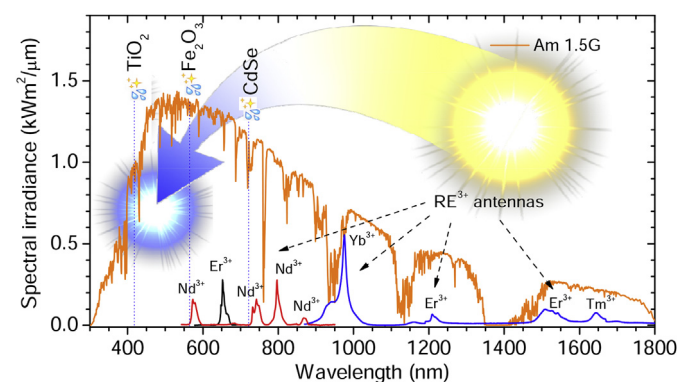
The nano-glass-ceramics presented in this work have been successfully synthesized by the authors via conventional melting and sol–gel techniques.  $\text{PbF}_2$ -nanocrystals based glass-ceramics have been prepared by conventional glass melting at 1050 °C for 2 h using the following composition in mol%: 30 $\text{SiO}_2$ , 15 $\text{Al}_2\text{O}_3$ , 29 $\text{CdF}_2$ , 22 $\text{PbF}_2$ , 3 $\text{YF}_3$  and 1 $\text{NdF}_3$ , and finally casting the melt into a slab on a stainless steel plate at room temperature. The transparent oxyfluoride glass ceramics were obtained just by thermal treatment of the glass at 470 °C for 24 h to precipitate nanocrystallites without loss of transparency. On the other hand,  $\text{NaYF}_4$ ,  $\text{YF}_3$ ,  $\text{KYF}_4$  nanocrystals based glass-ceramics have been prepared by sol–gel technique from silica glasses with compositions: 95 $\text{SiO}_2$ –5 $\text{NaYF}_4$  co-doped with 0.1 mol% of  $\text{Er}^{3+}$  and 0.3 mol% of  $\text{Yb}^{3+}$ ; 90 $\text{SiO}_2$ –10 $\text{YF}_3$  co-doped with 0.1 mol% of  $\text{Tm}^{3+}$  and 1.5 mol% of  $\text{Yb}^{3+}$ ; and 95 $\text{SiO}_2$ –5 $\text{KYF}_4$  co-doped with 1.2 $\text{Yb}^{3+}$ –0.1 $\text{Tm}^{3+}$  and 1.2 $\text{Yb}^{3+}$ –0.1 $\text{Ho}^{3+}$ , respectively. A mixed solution of tetraethoxysilane, ethanol,  $\text{H}_2\text{O}$ , acetic acid and potassium, yttrium, sodium and RE acetates as other components source. The resultant homogeneous solution, stirred vigorously for 1 h at room temperature, was leaved in a sealed container at 35 °C for several days to obtain a highly transparent gel, which were dried by a slow evaporation of residual water and solvent. Finally, these sol–gel glasses were heat-treated in air at temperatures between 675 and 700 °C in order to achieve controlled precipitation of fluoride nanocrystals. The RE doping ions are mainly residing in the low-phonon energy nanocrystalline fluoride environment ( $\text{PbF}_2$ ,  $\text{NaYF}_4$ ,  $\text{YF}_3$ ,  $\text{KYF}_4$ ) which are embedded into a silica oxide matrix, and thus constituting the nano-glass-

ceramics. Optical absorption measurements were performed on a Perkin Elmer Lambda 9 spectrophotometer in the VIS and NIR range. Up-conversion measurements were carried out with a continuous wave laser diode at 980 nm with a power up to 300 mW, collimated using a lens with a focal length of 4.51 mm and 0.55 of numerical aperture. And for 740 and 800 nm excitation, a continuous wave tuneable Ti:sapphire laser with 200 mW pump power was used. A 50 mm lens was used to focus the collimated laser beam over the sample. Detection was obtained through a 0.25 m monochromator equipped with a photomultiplier. CCD digital camera was used to take colour pictures of up-conversion luminescence emitted by the samples. All spectra were collected at room temperature and corrected by the instrumental response. Transmission electron microscopy (TEM) images were taken by using a JEOL JEM 3000F field emission electron microscope under a working voltage of 300 kV, allowing us to achieve a point-to-point resolution of 0.17 nm. Specimens were prepared by dispersing the fine powder, obtaining by grinding the bulk sample, in acetone with ultrasonic agitation and dropping onto carbon-coated copper grids. A selected area of the TEM image was mathematically filtered by means of Fast Fourier Transform (FFT) analysis resulting in power spectra pattern, corresponding to the eigen-frequencies of the observed nanocrystals. Further, the relevant frequencies were selected to filter the noise in the zoomed areas of the images in order to produce higher contrast of the atomic planes of the observed nanocrystals.

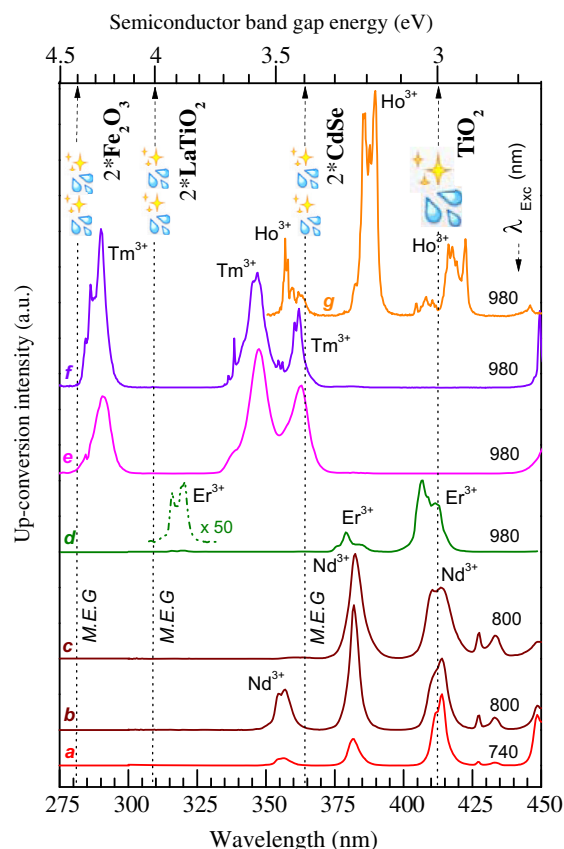
### 3. Results and discussion

In our bio-inspired scheme, RE-doped nanocrystals would act as light harvesters of the long red and near-infrared tail of the sun, as the antennas of chloroplasts do in plants, giving rise to intense UV and blue up-conversion emissions, and therefore, enabling water-splitting at semiconductor surface. These nano-plasts will lead the way to turn the sun into blue.

To experimentally support this blue-shifting photon approach we present next absorption spectra and subsequent very intense UV-blue up-conversion emissions in Figs. 1 and 2. Fig. 1 represents the standard incident solar spectrum AM 1.5G along with main absorption bands of selected RE-doping species in the red and near-infrared range; in particular for  $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions. Position of band gaps for several photo-catalytic semiconductor materials, such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CdSe}$  are also depicted. The



**Fig. 1.** Solar irradiation standard spectrum (AM 1.5G) along with main absorption bands of rare-earth (RE) ions ( $\text{Nd}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$ ). Position of band-gaps for several photocatalytic semiconductor materials, such as  $\text{TiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{CdSe}$  are also depicted. The RE ions would act as harvesting antennas to collect the maximum number of photons from red and NIR range and then, after suitable energy transfer processes, high intense UV and blue up-conversion emissions will be obtained, represented by the yellow to blue sun arrow shift. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 2.** Up-conversion spectra in the UV-blue region of RE-doped oxyfluoride nano-glass-ceramics synthesized by the authors comprising  $\text{PbF}_2$  (a,b,c),  $\text{NaYF}_4$  (d),  $\text{YF}_3$  (e) and  $\text{KYF}_4$  (f,g) nanocrystals, under red and near-infrared excitation as labelled in nm. Experimental measurements details are explained in the text. These high energetic emissions bridge the energy gap of main water-splitting semiconductor electrodes as depicted; even twice the gap thus eventually enabling multiple exciton generation (MEG) effects. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

trivalent lanthanide ions (RE) would act as harvesting antennas to collect the maximum number of photons reaching the semiconductor electrode in the photo-electrochemical (PEC) cell. Then, after suitable energy transfer processes, high intense UV and blue up-conversion emissions are obtained. Corresponding up-conversion spectra under different red and near-infrared excitation wavelengths are presented in Fig. 2 for different oxyfluoride nano-glass-ceramics developed by the authors [19,25–28] and described in detail in the Experimental section. It can be clearly seen how these up-conversion emissions can bridge the band gap of most important semiconductor electrodes used in water-splitting, such as  $\text{TiO}_2$ ,  $\text{CdSe}$ ,  $\text{LaTiO}_2$  and  $\text{Fe}_2\text{O}_3$ .

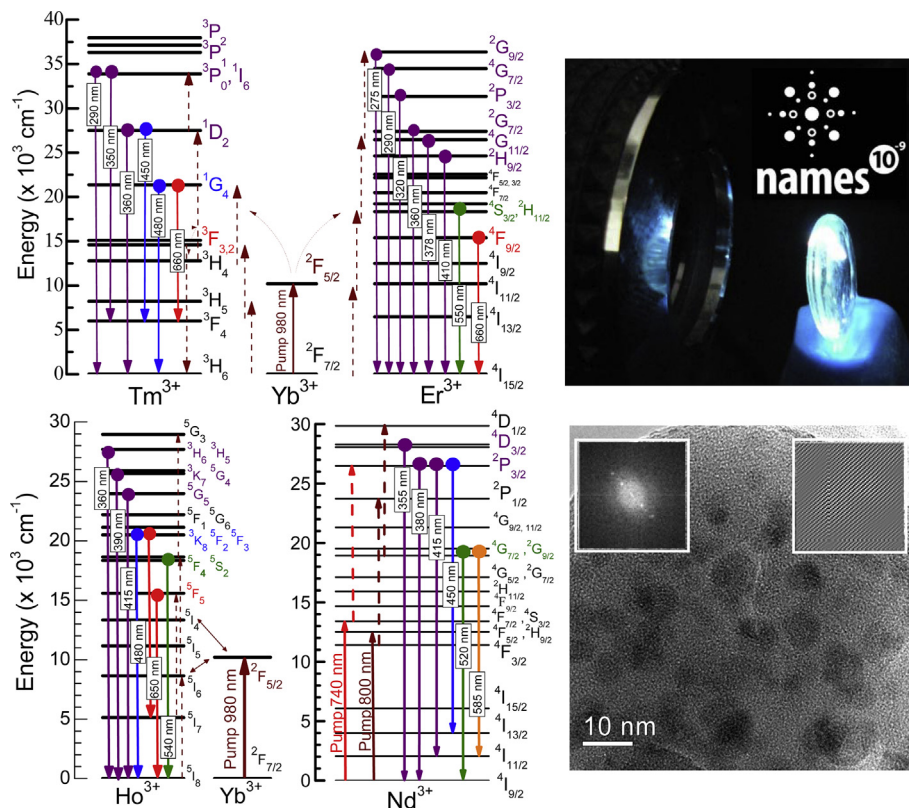
These UV-blue up-conversion emissions open the way to optimize single photon processes to split water without external bias, employing very wide band gap semiconductor materials, which unfortunately absorb only the small UV part of the solar spectrum resulting in low conversion efficiencies. The quantified overall efficiency of the infrared to UV and visible up-conversion processes in the presented nano-glass-ceramics was found to be significantly large. For instance, in the  $\text{YF}_3$ -based sol-gel derived nano-glass-ceramics (Fig. 2, curve e), 27% of the excitation photons involved in the up-conversion processes take to UV emissions, and the  $\text{PbF}_2$ -based conventional melting nano-glass-ceramics exhibited an up-conversion luminescence yield of 22% under 980 pump [28,29]. In fact, the unusual very efficient high energy up-conversion emissions (275–390 nm UV range, see Fig. 2), displayed by these nano-structured

samples, are significantly stronger than those recently reported in literature [11–13], and therefore represents a very promising step forward to utilize more solar radiation. In particular, the UV up-conversion emissions presented in this work are quite more intense than those observed in the  $\text{Yb}^{3+}\text{--Tm}^{3+}$  co-doped  $\text{Y}_2\text{O}_3$  nanocrystals agent utilized by T. Li et al. [12] for the photocatalytic decomposition of methylene orange, and also stronger than those corresponding to the  $\text{NaYF}_4\text{:Yb}^{3+}\text{--Tm}^{3+}/\text{CdS}$  nano-composite for methylene blue and rhodamine B degradation [11]. Hence this blue-shifting of solar spectrum would boost PEC hydrogen production, even enhancing spectral response of multijunction amorphous silicon (3jn-a-Si) used in outstanding artificial leaves [5,6,30], and therefore extending the photo-catalytic action beyond silicon gap due to significant RE ions absorption in the near-infrared range, see Fig. 1. Moreover, the approach presented here also puts forward an advantageous step to the sub-band gap photoaction response described lately by R. S. Khayzer et al. [14], since wavelength range for harvesting unused portions of sunlight is substantially larger in our case and also the use of organic complex species is avoided.

It should be also mentioned that the use of heavy rare-earth elements (HREE) proposed in our system (i.e. Ho, Er, Tm and Yb) also brings up an important benefit since their use is highly convenient for equilibrating the current balance problem. The demand for the different RE should be in agreement with their abundance ratios to avoid surpluses of certain metals that would result in imbalances of the markets. This balance problem implicates that the industry is ought to find new applications for less commonly used HREE that are obtained in excess in the manufacture process, and therefore lowering the price for any REE as the production costs are shared by all the elements [31].

Moreover, the observed highest energetic emissions beyond 3.4 eV, i.e. for wavelengths shorter than 280 and 365 nm, can bridge twice the gap of  $\text{Fe}_2\text{O}_3$  and CdSe respectively. This would allow to implement a process called Multiple Exciton Generation (MEG), also known as carrier multiplication [32], for exceeding 100% efficiency, whereby a single absorbed photon of appropriately high energy can produce more than one electron-hole pair, two for the price of one!, as demonstrated in a recent work by NREL in quantum-dot solar cells [33]. In that paper, Semonin et al. [33] reported the first solar cell with an external quantum efficiency with a peak value of 114% when photoexcited with photons from the high energy region of the solar spectrum. Other semiconductor electrodes with different energy gaps as those illustrated in Figs. 1 and 2 would be used in our photolysis system to obtain very high efficiencies due to multiple electron-hole generation via MEG effects under single UV-blue photon excitation.

The involved energy levels of different RE ions present in the studied nano-glass-ceramics are depicted in Fig. 3, i.e.  $\text{Yb}^{3+}\text{--Er}^{3+}$ ,  $\text{Yb}^{3+}\text{--Tm}^{3+}$ ,  $\text{Yb}^{3+}\text{--Ho}^{3+}$  couples and  $\text{Nd}^{3+}$  ions, displaying main up-conversion emissions along with their corresponding energy transfer up-conversion mechanisms under 740, 800 and 980 nm pump. As it can be seen, the  $\text{Yb}^{3+}$  ions mostly act as efficient NIR antenna because it is one of the best known suitable sensitizer for others RE ions, such as  $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$ , under IR radiation due to its particular energy level diagram with a unique long lifetime excited level with a large absorption cross section around  $1\text{ }\mu\text{m}$  ( $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$  transition) resonant with many inexpensive laser diodes, as it can be seen in Fig. 1. This intense absorption of  $\text{Yb}^{3+}$  and the subsequent efficient energy transfer to the activator ions ( $\text{Ho}^{3+}$ ,  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$ ), makes the here selected RE couples very efficient up-conversion systems, giving



**Fig. 3.** Energy level diagrams along with mechanisms and main up-conversion emissions for the  $\text{Yb}^{3+}\text{--Er}^{3+}$ ,  $\text{Yb}^{3+}\text{--Tm}^{3+}$ ,  $\text{Yb}^{3+}\text{--Ho}^{3+}$  couples and  $\text{Nd}^{3+}$  ions. CCD photograph of blue emissions coming from  $\text{Yb}^{3+}\text{--Tm}^{3+}$ -doped  $\text{PbF}_2$ -nanocrystal based glass-ceramics and TEM image corresponding to sol-gel derived nano-glass-ceramics comprising  $\text{KYF}_4$  nanocrystals are included. FFT filtered image of a single nanocrystal is also included. The names10<sup>9</sup> logo of our research group, [www.names-ull.es](http://www.names-ull.es) (names, nanomaterials and spectroscopy), is also presented.

rise to UV–vis light through NIR radiation. Moreover the efficient green and red visible up-conversion emissions also exhibited in these RE-doped nano-glass-ceramics [19,25–28] (depicted with corresponding transition wavelengths in Fig. 3) would also increase water-splitting activity of red metallic oxide photo-catalysts [9,10] and of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (haematite) just appeared in literature [13]. In addition a CCD photograph is also included in Fig. 3 as an example of high intense blue up-conversion emissions coming from Yb<sup>3+</sup>–Tm<sup>3+</sup>-doped PbF<sub>2</sub> nanocrystals residing into the studied samples. Even more important are the emissions not seen by the human eye in the photograph, i.e. the intense UV up-conversion emissions in the 275–390 nm range (see Fig. 2), of primordial interest for bridging the large band gap of most important semiconductor electrodes used in water-splitting, such as TiO<sub>2</sub>. Finally we have also included in Fig. 3, a Transmission Electron Microscopy (TEM) photograph as an illustrative pattern of the nanostructured character of the samples presented in this work. In particular the displayed TEM image corresponds to the KYF<sub>4</sub>-based sol–gel derived nano-glass-ceramics (Fig. 2, curve f and g), revealing dark spherical nanocrystals clearly distinguished over the grey background, related to the crystalline and the glassy phase, respectively. Inset includes also a FFT filtered image of a single nanocrystal.

We should mention that further development of proof-of-concept tests pursuing optimum performance of a proposed up-conversion powered photo-electrochemical (PEC) water-splitting cell [34], incorporating our RE-doped up-converter oxyfluoride nano-glass-ceramics, is currently being conducted by the authors [35].

#### 4. Conclusions

In summary here we report on efficient spectral UV and blue up-conversion processes in rare-earth doped nano-glass-ceramics as an interesting approach to assist long wavelength light harvesting of solar irradiation. This would extend the photo-catalytic response of water-splitting semiconductor electrodes used in a photo-electrochemical cell to the red and near-infrared region and thus overcoming the drawback of large band-gap materials requirement which only absorb a small fraction of incident solar light.

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